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Dated 24 July 2000

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Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

08 SEP 1999

The Patent Office
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NP9 1RH

1. Your reference

PH99052G1

2. Patent application number
(The Patent Office will fill in this part)

0012090.7

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Aventis Agriculture Limited
Fyfield Road
Ongar
Essex CM5 0HW

Patents ADP number *(if you know it)*

7901929001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

New Herbicidal Compositions

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Patent Department
Aventis Agriculture Limited
Fyfield Road
Ongar
Essex CM5 0HW

Patents ADP number *(if you know it)*

7901929002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*
9921220.1	08.09.1999

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

New Herbicidal Compositions

Background of the Invention

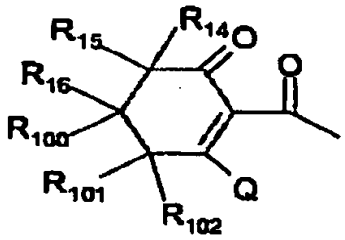
The present invention relates to the safening of herbicidal compounds, in particular the safening of benzoylisoxazole and/or dione derivatives which are useful for the growing of crops in particular for maize (*Zea mays*) and to compositions useful for such treatment.

Discussion of Related Art

An important factor influencing the usefulness of a given herbicide is its selectivity toward crops. In some cases, a beneficial crop is susceptible to the effects of a herbicide when applied at application rates needed to control weed growth. In addition, certain herbicidal compounds are phytotoxic to some weed species but not to others. This may render such herbicides unsuitable for controlling weeds in the presence of certain crops. To be effective, a herbicide must cause minimal damage (preferably no damage) to the beneficial crop while maximising the damage to weed species which infest the locus of the crop. Reduction in herbicidal injury to crops without an unacceptable reduction in the herbicidal action can be accomplished by the use of crop protectants known as "antidotes" or "safeners".

Identification of an antidote which safens a herbicide in crops is a complicated task. The precise mechanism by which an antidote reduces herbicidal crop injury has not been established. In general, the safening effect of a compound is specific to the herbicidal partner and the crop where the active ingredients are applied.

Benzoylisoxazoles are known to possess herbicidal properties for example, European Patent Publication Nos. 0418175, 0487357, 0527036 and 0560482. European Patent Publication Nos. 0496630, 0496631, 0625505 and 0625508 disclose certain dione derivatives possessing herbicidal properties. In general such herbicides are very active against broad-leafed and grass weeds by pre- and/or post-emergence application. The method of controlling vegetation with these compounds comprises applying a herbicidally effective amount of the compounds, usually with an inert carrier or diluent, to the area where herbicidal control is desired. However, the herbicidal benzoylisoxazole and/or dione compounds have been found in some instances to adversely affect or interfere with the



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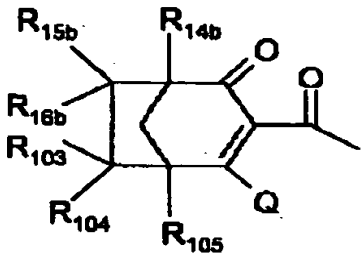

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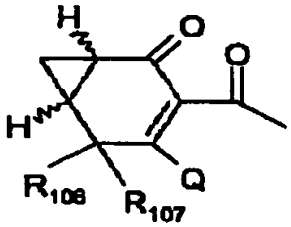

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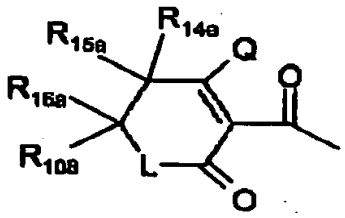
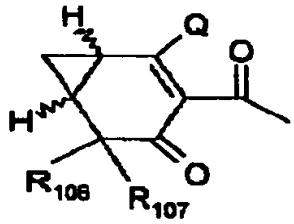
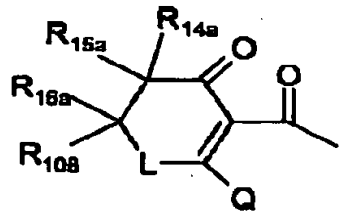


(A-7)

or a corresponding formula (A-6a) or (A-7a):



(A-6a)



(A-7a)

in which the position of the carbonyl group and the group Q are reversed and the double bond in the ring is attached to the carbon atom attached to the group Q;

R is a hydrogen atom or a halogen atom; a straight- or branched chain alkyl, alkenyl or alkynyl group containing from one to six carbon atoms which is optionally substituted by one or more halogen atoms; a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R^5, one or more halogen atoms or a group $-CO_2R^3$; or a group selected from $-CO_2R^3$, $-COR^5$, cyano, nitro, $-CONR^3R^4$ and $-S(O)_kR^{13}$;

R^1 is a straight- or branched-chain alkyl, alkenyl or alkynyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms; or a cycloalkyl group containing from three to six carbon atoms optionally substituted by one or more groups R^5 or ne or more halogen atoms;

R^8, R^9 and R^{10} are each a hydrogen atom or R^6;

R^{11} and R^{12} are each a hydrogen atom or R^5;

R^{13} and R^{111} are each a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

Q is hydroxy, C1-6 alkoxy, OR^{112}, SR^{112} or SR^{111};

L is oxygen or NR^{109};

R^{14}, R^{14a}, R^{14b}, R^{15}, R^{15a}, R^{15b}, R^{16}, R^{16a}, R^{16b}, R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, R^{107} and R^{108} are each the same or different groups selected from hydrogen, R^{110}, $-(CH_2)_uCO_2R^{109}$, halogen, cyano, C1-6 alkoxy, $-(CH_2)_x$-[phenyl optionally substituted by from one to five groups R^{113} which may be the same or different], and cycloalkyl containing from three to six carbon atoms optionally substituted by C1-6 alkyl or $-S(O)_pR^{111}$;

R^{112} is phenyl optionally substituted by from one to five groups selected from halogen, C1-6 alkyl, C1-6 haloalkyl, C1-6 alkoxy and nitro;

R^{113} is a group selected from halogen, R^{114}, nitro, cyano, $-CO_2R^{115}$, $-S(O)_pR^{111}$, $-OR^{111}$ and $-NR^{115}R^{116}$;

R^{114} is a straight- or branched- chain alkyl group containing one to three carbon atoms optionally substituted by one or more halogen atoms;

R^{115} and R^{116} which may be the same or different, are each a hydrogen atom or R^{110};

p, q and u are each independently zero, one or two;

k and m are each one, two or three;

x is zero or one;

y is an integer from one to four; when y is greater than one, the groups R^9 and R^{10} may be the same or different;

or an agriculturally acceptable salt or metal complex thereof; which method comprises applying to the locus of the crop, preferably before the herbicidal compound, an antidotally effective amount of an antidote compound, and optional partner herbicide.

In the definitions of symbols in this specification including th accompanying claims unless otherwise specified the following definiti ns generally apply to the radicals in the formulae (I), (Ia) and (Ib) below:-

'halogen' means a fluorine, chlorine, bromine or iodine atom; and

alkyl groups and moieties are straight or branched chain and contain from 1 to 6 carbon atoms.

Preferably A is a group of formula (A-I), (A-2), (A-3) or (A-4) (compounds of formula (A-1) are most preferred).

The benzoyl ring of the compounds of formula (I) is preferably 2,4-disubstituted, 2,3-disubstituted or 2,3,4-trisubstituted.

Preferably in formulae (A-4) to (A-7), the groups R^{14}, R^{15}, R^{16}, R^{100}, R^{101}, R^{102}, R^{14a}, R^{15a}, R^{16a}, R^{103}, R^{14b}, R^{15b}, R^{16b}, R^{104}, R^{105} and R^{108} are each hydrogen or lower alkyl (preferably hydrogen, methyl or ethyl); L (in A-7a) is NH; and Q is hydroxy or -S-phenyl.

Compounds of formula (I) in which A is (A-1),(A-2) or (A-3); R is hydrogen or $-CO_2R^3$ (in A-1 or A-2) wherein R^3 is a straight- or branched chain alkyl group containing up to three carbon atoms; and R^1 is cyclopropyl are preferred.

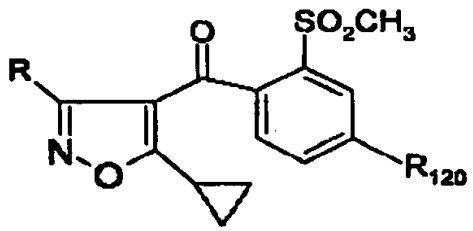
A further preferred class of compounds of formula (I) wherein A is (A-1) are those wherein:

R is hydrogen or $-CO_2Et$;

R^1 is cyclopropyl;

and two groups R^2, on adjacent carbon atoms of the phenyl ring may, together with the carbon atoms to which they are attached, combine to form a 5 or 6 membered saturated or unsaturated heterocyclic ring which is fused to the 2,3 or 3,4 positions of the benzoyl ring; wherein the heterocyclic ring contains two hetero atoms selected from sulphur and oxygen which are attached to the 2 and 3, or 3 and 4 positions of the benzoyl ring; and in which the 4-substituent of the benzoyl ring is halogen or $S(O)_pMe$, or the 2-substituent of the benzoyl ring is methyl, $S(O)_pMe$ or $-CH_2S(O)_qMe$ respectively; and optionally the heterocyclic ring may be substituted by one or more halogen atoms.

A further preferred class of compounds of formula (I) are those wherein A is (A-1); R is hydrogen or $-CO_2Et$; R^1 is cyclopropyl; R^2 is a halogen atom or a

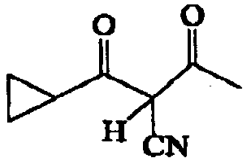


(Ib)

wherein R^{120} is chlorine, bromine or trifluoromethyl; and

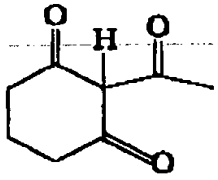
R is hydrogen or $-CO_2Et$.

Preferred diones are those in which a substituted phenyl ring as defined in formula (I); (Ia); or (Ib), is attached to a grouping;



Such diones in which the phenyl ring is substituted by two groups independently selected from halogen, alkyl, $S(O)_p$alkyl (p = 0, 1 or 2) and haloalkyl are also preferred.

Preferred triones are those in which a substituted phenyl ring, as defined above, is attached to a grouping;



The following compounds of formula (I) are among the most preferred for use in the present invention:

5-cyclopropyl-4-[2-chloro-3-ethoxy-4-(ethylsulphonyl)benzoyl]isoxazole;

4-(4-chloro-2-methylsulphonylbenzoyl)-5-cyclopropylisoxazole;

5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)isoxazole;

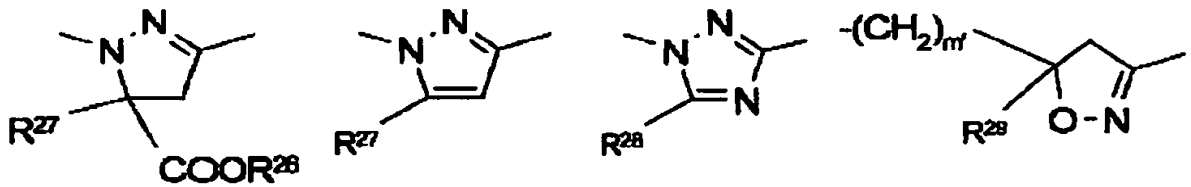
4-(4-bromo-2-methylsulphonylbenzoyl)-5-cyclopropylisoxazole;

5-cyclopropyl-4-[4-fluoro-3-methoxy-2-(methylsulphonyl)benzoyl]isoxazole;

4-(4-bromo-2-methylsulphonylmethylbenzoyl)-5-cyclopropylisoxazole;

ethyl 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)isoxazole-3-carboxylate;

W is an unsubstituted or substituted divalent heterocyclic radical selected from the group of the partially unsaturated r aromatic five-membered heterocyclic rings which have 1 to 3 hetero ring atoms of the N or O type, where the ring contains at least one N atom and not more than one O atom, preferably a radical selected from the group consisting of (W1) to (W4),



(W1) (W2) (W3) (W4)

m' is zero or 1;

R^{17} and R^{18} are the same or different halogen, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, nitro or (C_1-C_4)-haloalkyl;

R^{19} and R^{20} are the same or different OR^{24}, SR^{24} or $NR^{24}R^{25}$ or a saturated or unsaturated 3- to 7-membered heterocycle having at least one N atom and up to 3 hetero atoms, preferably from the group selected from O and S, which is linked to the carbonyl group in (II) or (III) via the N atom and is unsubstituted or substituted by radicals selected from the group consisting of (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy or optionally substituted phenyl, preferably a radical of the formula OR^{24}, NHR^{25} or $N(CH_3)_2$, in particular of the formula OR^{24};

R^{24} is hydrogen or an unsubstituted or substituted aliphatic hydrocarbon radical, preferably having a total of 1 to 18 C atoms;

R^{25} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_8)-alkoxy or substituted or unsubstituted phenyl;

R^{26} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_8)-haloalkyl, (C_1-C_4)-alkoxy-(C_1-C_4)-alkyl, (C_1-C_8)-hydroxyalkyl, (C_3-C_{12})-cycloalkyl or tri-(C_1-C_4)-alkyl-silyl; and

R^{27}, R^{28}, R^{29} are the same or different hydrogen, (C_1-C_8)-alkyl, (C_1-C_8)-haloalkyl, (C_3-C_{12})-cycloalkyl or substituted or unsubstituted phenyl;

b) one or more compounds selected from:

4,6-dichloro-2-phenylpyrimidine (fenclorim),

benzyl 2-chloro-4-trifluor methyl-1,3-thiazole-5-carboxylate (fluraz le),

N-(4-methylphenyl)-N'-(1-methyl-1-phenylethyl)urea (daimuron),

moiety preferably having 1 to 20 carbon atoms and a carbon-containing radical R^{30} inclusive of substituents preferably having 1 to 30 carbon atoms;
R^{31} is hydrogen or (C_1-C_4)-alkyl, preferably hydrogen, or
R^{30} and R^{31} together with the group of the formula -CO-N- are the residue of a 3- to 8-membered saturated or unsaturated ring;
R^{32} is identical or different halogen, cyano, nitro, amino, hydroxyl, carboxyl, formyl, $CONH_2$, SO_2NH_2 or a radical of the formula Z^b-R^b;
R^{33} is hydrogen or (C_1-C_4)-alkyl, preferably H;
R^{34} is the same or different halogen, cyano, nitro, amino, hydroxyl, carboxyl, CHO, $CONH_2$, SO_2NH_2 or a radical of the formula Z^c-R^c;
R^a is a hydrocarbon radical or a heterocyclyl radical, which radicals are unsubstituted or substituted by one or more groups which may be the same or different selected from halogen, cyano, nitro, amino, hydroxyl, mono- and di-[(C_1-C_4)-alkyl]amino, or an alkyl radical in which a plurality, preferably 2 or 3, non-adjacent CH_2 groups are in each case replaced by one oxygen atom;
R^b and R^c are the same or different hydrocarbon radical or heterocyclyl radical, which radicals are unsubstituted or substituted by one or more groups which may be the same or different selected from halogen, cyano, nitro, amino, hydroxyl, phosphoryl, halo-(C_1-C_4)-alkoxy, mono- and di-[(C_1-C_4)-alkyl]amino, or an alkyl radical in which a plurality, preferably 2 or 3, non-adjacent CH_2 groups are replaced in each case by one oxygen atom;
Z^a is a divalent group of the formula O, S, CO, CS, CO-O, CO-S, O-CO, S-CO, SO, SO_2, NR*, CO-NR*, NR*-CO, SO_2-NR* or NR*-SO_2, the bond given on the right-hand side of each of the divalent groups being the bond to the radical R^a, and the radicals R* are each independently H, (C_1-C_4)-alkyl or halo-(C_1-C_4)-alkyl;
Z^b and Z^c are each independently a direct bond or a divalent group of the formula O, S, CO, CS, CO-O, CO-S, O-CO, S-CO, SO, SO_2, NR*, SO_2-NR*, NR*-SO_2, CO-NR* or NR*-CO, where, in asymmetrical divalent groups, the atom on the right-hand side is linked to the radical R^b or R^c and where the radicals R* are each independently H, (C_1-C_4)-alkyl or halo-(C_1-C_4)-alkyl;
n is an integer from zero to 4, preferably zero, 1 or 2, in particular zero or 1, and
t is an integer from zero to 5, preferably zero, 1, 2 or 3, in particular zero, 1 or 2;

d) acylsulfamoylbenzamides of the formula (V), or salts thereof:

Z^d is a divalent unit selected from the group consisting of O, S, CO, CS, C(O)O, C(O)S, SO, SO_2, NR^*, $C(O)NR^*$ or SO_2NR^*;

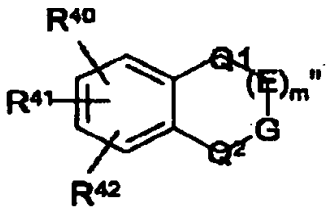
Z^e and Z^f are the same or different and are a direct bond or a divalent unit selected from O, S, CO, CS, C(O)O, C(O)S, SO, SO_2, NR^*, SO_2NR^* and $C(O)NR^*$;

R^* is hydrogen, (C_1-C_4)-alkyl or (C_1-C_4)-haloalkyl;

s is an integer from zero to 4, and

o is an integer from zero to 5 when X is CH, or is an integer from zero to 4 when X is N;

e) compounds of the formula (VI):



(VI)

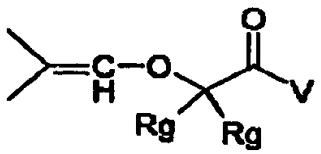
wherein:

R^{40} is H, (C_1-C_4)-alkyl, (C_1-C_4)-alkyl substituted by (C_1-C_4)-alkyl-X^4 or (C_1-C_4)-haloalkyl-X^4, (C_1-C_4)-haloalkyl, NO_2, CN, -COO-R^{43}, NR_2^{44}, $SO_2NR_2^{45}$ or $CONR_2^{46}$;

R^{41} is H, halogen, (C_1-C_4)-alkyl, CF_3, (C_1-C_4)-alkoxy or (C_1-C_4)-haloalkoxy;

R^{42} is H, halogen or (C_1-C_4)-alkyl;

Q^1, Q^2, E and G are the same or different O, S, CR_2^{47}, CO, NR^{48} or a group of the formula (VII):



(VII)

with the proviso that:

i) at least one of the groups Q^1, Q^2, E, G is a carbonyl group, that exactly one of these groups is a radical of the formula (VII) and that the group of the formula (VII) is adjacent to a carbonyl gr up, and

ii) two adjacent groups Q^1, Q^2, E and G cannot simultaneously be oxygen;

straight-chain or branched in the carbon skeleton. Alkyl radicals, also the composite meanings such as alkoxy, haloalkyl and the like, preferably have 1 to 4 carbon atoms and are, for example, methyl, ethyl, n- or i-propyl or n-, i-, t- or 2-butyl. Alkenyl and alkynyl radicals have the meanings of the unsaturated radicals which are possible which correspond to the alkyl radicals; alkenyl is, for example, allyl, 1-methylprop-2-en-1-yl, 2-methylprop-2-en-1-yl, but-2-en-1-yl, but-3-en-1-yl, 1-methylbut-3-en-1-yl and 1-methylbut-2-en-1-yl. Alkynyl is, for example, propargyl, but-2-yn-1-yl, but-3-yn-1-yl, 1-methylbut-3-yn-1-yl. "(C_1-C_4)-Alkyl" is the abbreviation for alkyl having 1 to 4 carbon atoms; the same applies analogously to other general definitions of radicals, where the range of the possible number of carbon atoms is indicated in brackets.

Cycloalkyl is, preferably, a cyclic alkyl radical having 3 to 8, preferably 3 to 7, especially preferably 3 to 6, carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Cycloalkenyl and cycloalkinyl denote corresponding unsaturated compounds.

Halogen is fluorine, chlorine, bromine or iodine. Haloalkyl, haloalkenyl and haloalkynyl are alkyl, alkenyl or alkynyl which are partially or fully substituted by halogen, preferably by fluorine, chlorine and/or bromine, in particular by fluorine or chlorine, for example CF_3, CHF_2, CH_2F, CF_3CF_2, CH_2FCHCl, CCl_3, $CHCl_2$, CH_2CH_2Cl. Haloalkoxy is, for example, OCF_3, $OCHF_2$, OCH_2F, CF_3CF_2O, OCH_2CF_3 and OCH_2CH_2Cl. This also applies analogously to other halogen-substituted radicals.

A hydrocarbon radical can be an aromatic or an aliphatic hydrocarbon radical, where an aliphatic hydrocarbon radical is generally a straight-chain or branched saturated or unsaturated hydrocarbon radical, preferably having 1 to 18, especially preferably 1 to 12, carbon atoms, for example alkyl, alkenyl or alkynyl. Aliphatic hydrocarbon radical preferably means alkyl, alkenyl or alkynyl having up to 12 carbon atoms; the same applies analogously to an aliphatic hydrocarbon radical in a hydrocarbon-oxy radical.

Aryl is generally a mono-, bi- or polycyclic aromatic system having by preference 6-20 carbon atoms, preferably 6 to 14 carbon atoms, especially preferably 6 t 10 carbon atoms, for example phenyl, naphthyl, tetrahydronaphthyl, indenyl, indanyl, pentalenyl and fluorenyl, especially preferably phenyl.

Heterocyclic ring, heterocyclic radical or heterocyclyl is a mono-, bi- or polycyclic

and, in the case of cyclic radicals, also alkyl and haloalkyl and the unsaturated aliphatic substituents which correspond to the abovementioned saturated hydrocarbon-containing substituents, preferably alkenyl, alkynyl, alkenyloxy and alkynyloxy. In the case of radicals having carbon atoms, those having 1 to 4 carbon atoms, in particular 1 or 2 carbon atoms, are preferred. As a rule, preferred substituents are those seelected from the group consisting of halogen, for example fluorine or chlorine, (C_1-C_4)-alkyl, preferably methyl or ethyl, (C_1-C_4)-haloalkyl, preferably trifluoromethyl, (C_1-C_4)-alkoxy, preferably methoxy or ethoxy, (C_1-C_4)-haloalkoxy, nitro and cyano. Especially preferred in this context are the substituents methyl, methoxy and chlorine.

Mono- or disubstituted amino is a chemically stable radical selected from the group of the substituted amino radicals which are N-substituted by, for example, one or two identical or different radicals selected from the group consisting of alkyl, alkoxy, acyl and aryl; preferably monoalkylamino, dialkylamino, acylamino, arylamino, N-alkyl-N-arylamino and N-heterocycles. Preferred in this context are alkyl radicals having 1 to 4 carbon atoms. By preference, aryl is phenyl. By preference, substituted aryl is substituted phenyl. The definition given further below applies to acyl, preferably (C_1-C_4)-alkanoyl. This also applies analogously to substituted hydroxylamino or hydrazino.

By preference, optionally substituted phenyl is phenyl which is unsubstituted or mono- or polysubstituted, preferably up to trisubstituted, in the case of halogen such as Cl and F also up to pentasubstituted, by identical or different radicals selected from the group consisting of halogen, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-haloalkyl, (C_1-C_4)-haloalkoxy and nitro, for example o-, m- and p-tolyl, dimethylphenyls, 2-, 3- and 4-chlorophenyl, 2-, 3- and 4-trifluoro- and -trichlorophenyl, 2,4-, 3,5-, 2,5- and 2,3-dichlorophenyl, o-, m- and p-methoxyphenyl.

An acyl radical is the radical of an organic acid having by preference up to 6 carbon atoms, for example the radical of a carboxylic acid and radicals of acids derived therefrom, such as thiocarboxylic acid, optionally N-substituted iminocarboxylic acids, or the radical of carbonic monoesters, optionally N-substituted carbamic acids, sulfonic acid, sulfinic acids, phoshonic acids, phosphinic acids. Acyl is, for example, formyl, alkylcarbonyl such as (C_1-C_4-alkyl)-carbonyl, phenylcarbonyl, it being possible for the phenyl ring to be substituted,

R^{51} is the same or different halogen, nitro, (C_1-C_4)-alkoxy and phenyl which is unsubstituted or substituted by one or more, preferably up to three, radicals R^{52};
R^{52} is the same or different halogen, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-haloalkyl, (C_1-C_4)-haloalkoxy or nitro;
R' is the same or different hydrogen, (C_1-C_8)-alkyl, phenyl which is unsubstituted or substituted by one or more, preferably up to three, radicals R^{52}, or two radicals R' together form a (C_2-C_8)-alkanediyl chain;
R'' is the same or different (C_1-C_4)-alkyl or two radicals R'' together form a (C_2-C_8)-alkanediyl chain;
R''' is hydrogen or (C_1-C_4)-alkyl; and
w is zero, 1, 2, 3, 4, 5 or 6.

Especially preferred are herbicide/antidote combinations according to the invention which comprise antidotes of the formula (II) and/or (III) where the symbols and indices have the following meanings:
R^{24} is hydrogen, (C_1-C_8)-alkyl or (C_3-C_7)-cycloalkyl, the above carbon-containing radicals being unsubstituted or mono- or polysubstituted by halogen or mono- or disubstituted, by preference monosubstituted, by radicals R^{50},
R^{50} is the same or different hydroxyl, (C_1-C_4)-alkoxy, carboxyl, (C_1-C_4)-alkoxycarbonyl, (C_2-C_6)-alkenyloxycarbonyl, (C_2-C_6)-alkynyloxycarbonyl, 1-(hydroxyimino)-(C_1-C_4)-alkyl, 1-[(C_1-C_4)-alkylimino]-(C_1-C_4)-alkyl and 1-[(C_1-C_4)-alkoxyimino]-(C_1-C_4)-alkyl; SiR'$_3$, O-N=CR'$_2$, N=CR'$_2$, NR'$_2$ and ONR'$_3$ where R' is identical or different hydrogen, (C_1-C_4)-alkyl or, as a pair, a (C_4-C_5)-alkanediyl chain,
R^{27}, R^{28} and R^{29} are the same or different hydrogen, (C_1-C_8)-alkyl, (C_1-C_8)-haloalkyl, (C_3-C_7)-cycloalkyl or phenyl which is unsubstituted or substituted by one or more groups selected from halogen, cyano, nitro, amino, mono- and di-[(C_1-C_4)-alkyl]-amino, (C_1-C_4)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-haloalkoxy, (C_1-C_4)-alkylthio and (C_1-C_4)-alkylsulfonyl;
R^{26} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_8)-haloalkyl, (C_1-C_4-alkoxy)-(C_1-C_4)-alkyl, (C_1-C_8)-hydroxyalkyl, (C_3-C_7)-cycloalkyl or tri-(C_1-C_4)-alkylsilyl,
R^{17} and R^{18} are the same or different halogen, methyl, ethyl, methoxy, ethoxy, (C_1 or C_2)-haloalkyl, by preference hydrogen, halogen or (C_1 or C_2)-haloalkyl.

R^{17} is halogen or (C_1-C_2)-haloalkyl;

n' is zero, 1, 2 or 3, where $(R^{17})_{n'}$ is by preference 2,4-Cl_2;

R^{18} is a radical of the formula OR^{24};

R^{24} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-hydroxyalkyl, (C_3-C_7)-cycloalkyl, (C_1-C_4)-alkoxy-(C_1-C_4)-alkyl or tri-(C_1-C_2)-alkylsilyl, by preference (C_1-C_4)-alkyl;

R^{27} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_4)-haloalkyl or (C_3-C_7)-cycloalkyl, by preference hydrogen or (C_1-C_4)-alkyl, and

R^{28} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-hydroxyalkyl, (C_3-C_7)-cycloalkyl, (C_1-C_4)-alkoxy-(C_1-C_4)-alkyl or tri-(C_1-C_2)-alkylsilyl, by preference hydrogen or (C_1-C_4)-alkyl.

Also especially preferred are herbicidal compositions comprising an antidote of the formula (II) where the symbols and indices have the following meanings:

W is (W2);

R^{17} is halogen or (C_1-C_2)-haloalkyl;

n' is zero, 1, 2 or 3, where $(R^{17})_{n'}$ is by preference 2,4-Cl_2;

R^{18} is a radical of the formula OR^{24};

R^{24} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-hydroxyalkyl, (C_3-C_7)-cycloalkyl, (C_1-C_4-alkoxy)-(C_1-C_4)-alkyl or tri-(C_1-C_2)-alkyl-silyl, by preference (C_1-C_4)-alkyl, and

R^{27} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_4)-haloalkyl, (C_3-C_7)-cycloalkyl or phenyl, by preference hydrogen or (C_1-C_4)-alkyl.

Also especially preferred are antidotes of the formula (II) where the symbols and indices have the following meanings:

W is (W3);

R^{17} is halogen or (C_1-C_2)-haloalkyl;

n' is zero, 1, 2 or 3, where $(R^{17})_n$ is by preference 2,4-Cl_2;

R^{18} is a radical of the formula OR^{24};

R^{24} is hydrogen, (C_1-C_8)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-hydroxyalkyl, (C_3-C_7)-cycloalkyl, (C_1-C_4)-alkoxy-(C_1-C_4)-alkyl or tri-(C_1-C_2)-alkylsilyl, by preference (C_1-C_4)-alkyl, and

R^{28} is (C_1-C_8)-alkyl or (C_1-C_4)-haloalkyl, by preference C_1-haloalkyl.

ethyl, i.e. ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl-(1H)-1,2,4-triazole-3-carboxylate (II-6); fenchlorazole, i.e. 1-(2,4-dichlorophenyl)-5-trichloromethyl-(1H)-1,2,4-triazole-3-carboxylic acid, and related compounds (see EP-A-0 174 562 and EP-A-0 346 620);

d) Compounds of the 5-benzyl- or 5-phenyl-2-isoxazoline-3-carboxylic acid type or the 5,5-diphenyl-2-isoxazoline-3-carboxylic acid type (where W = (W4)), by preference compounds such as ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate (II-7) or ethyl 5-phenyl-2-isoxazoline-3-carboxylate (II-8) and related compounds as they are described in WO-A- 91/08202, or ethyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (II-9), or 5,5-diphenyl-2-isoxazoline-3-carboxylic acid, or n-propyl 5,5-diphenyl-2-isoxazoline-carboxylate (II-10) or ethyl 5-(4-fluorophenyl)-5-phenyl-2-isoxazoline-3-carboxylate (II-11), as described in WO-A-95/07897.

e) Compounds of the 8-quinolinoxyacetic acid type, for example those of the formula (III) where $(R^{19})_{n'}$ = 5-Cl, $R^{20} = OR^{24}$ and T = CH_2, by preference the compounds
1-methyl (5-chloro-8-quinolinoxy)acetate (III-1),
1,3-dimethyl-but-1-yl (5-chloro-8-quinolinoxy)acetate (III-2),
4-allyloxybutyl (5-chloro-8-quinolinoxy)acetate (III-3),
1-allyloxyprop-2-yl (5-chloro-8-quinolinoxy)acetate (III-4),
ethyl (5-chloro-8-quinolinoxy)acetate (III-5),
methyl (5-chloro-8-quinolinoxy)acetate (III-6),
allyl (5-chloro-8-quinolinoxy)acetate (III-7),
2-(2-propylideneiminoxy)-1-ethyl (5-chloro-8-quinolinoxy)acetate (III-8),
2-oxo-prop-1-yl (5-chloro-8-quinolinoxy)acetate (III-9) and related compounds as they are described in EP-A-0 860 750, EP-A-0 094 349 and EP-A-0 191 736 or EP-A-0 492 366.

f) Compounds of the (5-chloro-8-quinolinoxy)malonic acid type, i.e. of the formula (III) where $(R^{19})_{n'}$ = 5-Cl, $R^{20} = OR^{24}$, T = -CH(COO-alkyl)-, by preference the compounds di thyl (5-chloro-8-quinolinoxy)malonate, diallyl (5-chloro-8-quinolinoxy)malonate, methyl ethyl (5-chloro-8-quinolinoxy)malonate and related compounds as they are described in EP-A-0 582 198.

R^{31} is hydrogen,

R^{32} is halogen, halo-(C_1-C_4)-alkyl, halo-(C_1-C_4)-alkoxy, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-alkylsulfonyl, (C_1-C_4)-alkoxycarbonyl or (C_1-C_4)-alkylcarbonyl, by preference halogen, (C_1-C_4)-haloalkyl such as trifluoromethyl, (C_1-C_4)-alkoxy, halo-(C_1-C_4)-alkoxy, (C_1-C_4)-alkoxycarbonyl or (C_1-C_4)-alkylsulfonyl,

R^{33} is hydrogen,

R^{34} is halogen, (C_1-C_4)-alkyl, halo-(C_1-C_4)-alkyl, halo-(C_1-C_4)-alkoxy, (C_3-C_6)-cycloalkyl, phenyl, (C_1-C_4)-alkoxy, cyano, (C_1-C_4)-alkylthio, (C_1-C_4)-alkylsulfynyl, (C_1-C_4)-alkylsulfonyl, (C_1-C_4)-alkoxycarbonyl or (C_1-C_4)-alkylcarbonyl, by preference halogen, (C_1-C_4)-alkyl, (C_1-C_4)-haloalkyl such as trifluoromethyl, halo-(C_1-C_4)-alkoxy, (C_1-C_4)-alkoxy or (C_1-C_4)-alkylthio,

n is zero, 1 or 2 and

t is 1 or 2.

Furthermore preferred are antidotes of the formula (V) in which

X^3 is CH;

R^{35} is hydrogen; or R^{35} is (C_1-C_8)-alkyl, (C_3-C_8)-cycloalkyl, (C_2-C_8)-alkenyl, (C_5-C_8)-cycloalkenyl, phenyl or 3- to 6-membered heterocyclyl having up to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, which radicals are optionally substituted by one or more groups which may be the same or different selected from halogen, (C_1-C_6)-alkoxy, (C_1-C_6)-haloalkoxy, (C_1-C_2)-alkylsulfynyl, (C_1-C_2)-alkylsulfonyl, (C_3-C_6)-cycloalkyl, (C_1-C_4)-alkoxycarbonyl, (C_1-C_4)-alkylcarbonyl and phenyl and in the case of cyclic radicals, also (C_1-C_4)-alkyl and (C_1-C_4)-haloalkyl;

R^{36} is hydrogen; or R^{36} is (C_1-C_8)-alkyl, (C_2-C_8)-alkenyl, (C_2-C_8)-alkynyl, which radicals are optionally substituted by one or more groups which may be the same or different selected from halogen, hydroxyl, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy and (C_1-C_4)-alkylthio;

R^{37} is halogen, (C_1-C_4)-haloalkyl, (C_1-C_4)-haloalkoxy, nitro, (C_1-C_4)-alkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-alkylsulfonyl, (C_1-C_4)-alkoxycarbonyl or (C_1-C_4)-alkylcarbonyl;

R^{38} is hydrogen;

R^{39} is halogen, nitro, (C_1-C_4)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-haloalkoxy, (C_3-C_6)-cycloalkyl, phenyl, (C_1-C_4)-alkoxy, cyano, (C_1-C_4)-alkylthio, (C_1-C_4)-alkylsulfinyl, (C_1-C_4)-alkylsulfonyl, (C_1-C_4)-alkoxycarbonyl or (C_1-C_4)-alkylcarbonyl;

dimepiperate, which is S-1-methyl-1-phenylethyl piperidine-1-carbothioate; 5,5-diphenylisoxazoline-3-carboxylic acid; and ethyl 5,5-diphenylisoxazoline-3-carboxylate (most preferably fenchlorazole; CMPI; 4-hydroxy-1-methyl-3-(1-1H-tetrazol-5-ylmethanoyl)-1H-quinolin-2-one; (S)-MBU and dimepiperate).

The mixtures of the invention may be used to obtain selective weed control with low crop injury in various crop plants such as maize, soybean, cotton, canola, sugar beet, potatoes, wheat, tobacco, rice and oil seed rape. Preferred crops include maize, sugar beet, cotton and canola. Particularly preferred crop species are maize and soybean, especially maize.

Effective weed control coupled with low crop injury is a result of treatment of a plant locus with a combination of a herbicidal benzoylisoxazole and/or dione derivative and an antidote compound in accordance with the method of the present invention. By application to the 'plant locus' is meant application, for example to the plant growing medium, such as soil, as well as to the seeds, emerging seedlings, roots, stems, leaves or other plant parts.

The phrase 'combination of a herbicidal isoxazole and/or dione derivative and an antidote compound' includes various methods of treatment. For example, the soil of a plant locus may be treated with a "tank-mix" composition containing a mixture of the herbicide and the antidote which is "in combination" , or the soil may be treated with the herbicide and antidote compounds separately so that the "combination" may be made on, or in the soil. After such treatments of the soil with a mixture of herbicide and antidote or by separate or sequential application of the herbicide and the antidote to the soil, the herbicide and antidote may be mixed into or incorporated into the soil either by mechanical mixing of the soil with implements or by "watering in" by rainfall or irrigation. The soil of a plant locus may also be treated with antidote by application of the antidote in a dispersible-concentrate form such as a granule. The granule may be applied to a furrow which is prepared for receipt of the crop seed and the herbicide may be applied to the plant locus either before or after in-furrow placement of the antidote-containing granule so that the herbicide and antidote form a "combination". Crop seed may be treated or coated with the antidote compound either while the crop seed is in-furrow just after seeding or, more commonly, the crop seed may be treated or coated with antidote prior to seeding into a furrow.

generally suitable, with a rate of about 0.01kgha^{-1} to 2kgha^{-1} being preferred, and with a rate of 0.005kgha^{-1} to 0.3kgha^{-1} being more preferred.

The amount of antidote used in the method of the invention varies according to a number of parameters including the particular antidote employed, the crop to be protected, the amount and rate of herbicide applied, and the edaphic and climatic conditions prevailing. Also, the selection of the specific antidotes for use in the method of the invention, the manner in which it is to be applied and the determination of the activity which is non-phytotoxic but antidotally effective, can be readily performed in accordance with common practice in the art.

The antidote is applied in combination with the herbicide in a non-phytotoxic antidotally effective amount. By "non-phytotoxic" is meant an amount of the antidote which causes at most minor or no injury to the desired crop species. By "antidotally-effective" is meant an antidote used in an amount which is effective as an antidote with the herbicide to decrease the extent of injury caused by the herbicide to the desired crop species.

The herbicide/safener combination according to the invention may also be employed for controlling harmful plants in crops of genetically engineered plants which are either known or still to be developed. As a rule, the transgenic plants are distinguished by particular, advantageous properties, for example by resistances to certain crop protection agents, resistances to plant diseases or pathogens causing plant diseases such as particular insects or microorganisms such as fungi, bacteria or viruses. Other particular properties relate for example, to the harvested material in terms of quantity, quality, storing properties, composition and specific constituents. Thus, transgenic plants are known which have an increased starch content or an altered starch quality, or those where the harvested material has a different fatty acid composition.

The use of the combinations according to the invention in economically important transgenic crops of useful plants and ornamentals, for example cereals such as wheat, barley, rye, oats, panic grasses, rice, cassava and maize or else crops of sugar beet, cotton, soya, oilseed rape, potatoes, tomatoes, peas and other types of vegetables.

When the combinations acc rding t the invention are applied in transgenic crops, effects n harmful plants to be observed in ther crops are frequently

Pre-em rgence activity of Compound A on maize in the presence of antidotes.

	g/ha of antidote	% phytotoxicity
Cpd A	63	15
Cpd A + mefenpyr-diethyl	63	8.75
Cpd A + fenchlorazole-ethyl	63	11.3
Cpd A + Antidote A	63	11.3
Cpd A + Antidote B	63	8.75

Post-emergence activity of Compound A (63g/ha) on maize in the presence of antidotes.

	g/ha of antidote	% phytotoxicity
Cpd A	63	27.5
Cpd A + mefenpyr-diethyl	63	25
Cpd A + fenchlorazole-ethyl	63	27.5
Cpd A + Antidote A	63	5
Cpd A + Antidote B	63	5

Post-emergence activity of Compound A (125g/ha) on maize in the presence of antidotes.

	g/h of antidote	% phytotoxicity
Cpd A	125	43
Cpd A + Antidote A	31	15
Cpd A + Antidote A	63	10
Cpd A + Antidote A	125	15
Cpd A + Antidote B	31	19
Cpd A + Antidote B	63	18
Cpd A + Antidote B	125	25

According to a further featur of the present invention, there are provided herbicidal compositions comprising:

condensation with ethylene oxide, alkali and alkaline earth metal salts of sulphuric acid est rs and sulphonic acids such as dinonyl- and dioctyl-sodium sulphono-succinates and alkali and alkaline earth metal salts of high molecular weight sulphonic acid derivatives such as sodium and calcium lignosulphonates.

Examples of suitable solid diluents or carriers are aluminium silicate, talc, calcined magnesia, kieselguhr, tricalcium phosphate, powdered cork, absorbent carbon black and clays such as kaolin and bentonite. Examples of suitable liquid diluents include water, acetophenone, cyclohexanone, isophorone, toluene, xylene, and mineral, animal, and vegetable oils (these diluents may be used alone or in combination).

Herbicidal compositions according to the present invention may also contain, if desired, conventional adjuvants such as adhesives, protective colloids, thickeners, penetrating agents, stabilisers, sequestering agents, anti-caking agents, colouring agents and corrosion inhibitors. These adjuvants may also serve as carriers or diluents.

Granular formulations may be prepared by absorbing the compounds of the present invention (dissolved in suitable solvents, which may, if desired, be volatile) onto the solid diluents or carriers in granular form and, if desired, evaporating the solvents, or by granulating compositions in powder form obtained as described above.

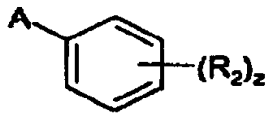
Powders, dispersible granules and liquid compositions in the form of concentrates may be diluted with water or other suitable diluents, for example mineral or vegetable oils, particularly in the case of liquid concentrates in which the diluent or carrier is an oil, to give compositions ready for use.

The wettable powders (or powders for spraying) usually contain from 20 to 95% of combination, and they usually contain, in addition to the solid vehicle, from 0 to 5% of a wetting agent, from 3 to 10% of a dispersant agent and if necessary, from 0 to 10% of one or more stabilisers and/or other additives such as penetrating agents, adhesives or anti-caking agents and colourings.

The aqueous suspension concentrates, which are applicable by spraying, are prepared in such a way as to obtain a stable fluid product (by fine grinding) which does not settle out and they usually contain from 10 to 75% of combination, from 0.5 to 15% of surface acting agents, from 0.1 to 10% of thixotropic agents, from 0 t 10% of suitable additives such as antifoams, corr sion

CLAIMS

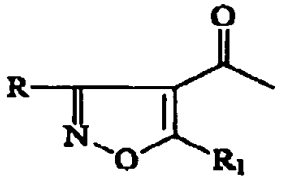
1. A method of reducing phytotoxicity to a crop (especially maize) at a locus caused by the application thereto of a herbicidal benzoylisoxazole and/or dione derivative of formula (I):



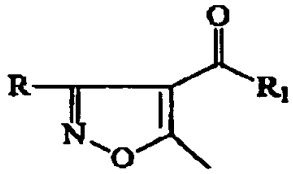
(I)

wherein:

A is a group (A-1) to (A-7):



(A-1)



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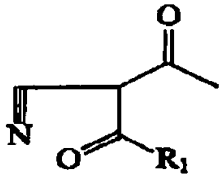

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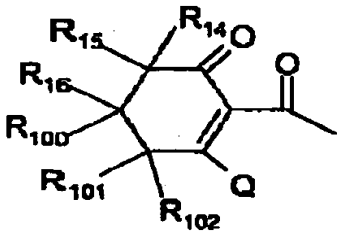

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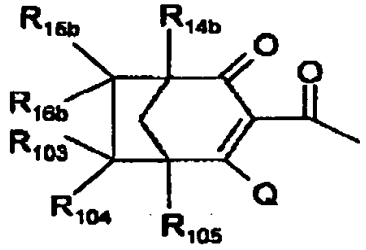

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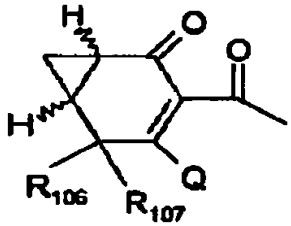
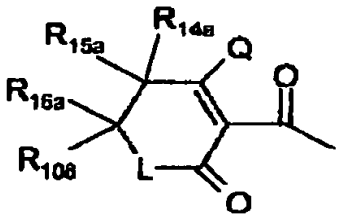


(A-6)



(A-7)

or a corresponding formula (A-6a) or (A-7a):

ther of), and $=NO-R^3$, it being understood that a sulphur atom, where present in the ring, may b in the form of a group -SO- or $-SO_2-$;

z is an integer from one to five: when z is greater than one the groups R^2 may be the same or different;

R^3, R^4 and R^{109} are each independently a hydrogen atom, or a straight- or branched chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

R^5 and R^{110} are each independently a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms or a straight- or branched-chain alkenyl or alkynyl group containing from two to six (preferably from three to six) carbon atoms which is optionally substituted by one or more halogen atoms;

R^6 and R^7, which may be the same or different, are each R^5; or phenyl optionally substituted by from one to five groups which may be the same or different selected from a halogen atom, a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms, nitro, cyano, $-CO_2R^5$, $-S(O)_pR^{13}$, $-NR^{11}NR^{12}$, $-OR^5$ and $-CONR^3R^4$;

R^8, R^9 and R^{10} are each a hydrogen atom or R^6;

R^{11} and R^{12} are each a hydrogen atom or R^5;

R^{13} and R^{111} are each a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

Q is hydroxy, C1-6 alkoxy, OR^{112}, SR^{112} or SR^{111};

L is oxygen or NR^{109};

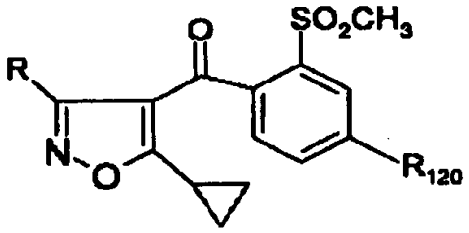
R^{14}, R^{14a}, R^{14b}, R^{15}, R^{15a}, R^{15b}, R^{16}, R^{16a}, R^{16b}, R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, R^{107} and R^{108} are each the same or different groups selected from hydrogen, R^{110}, $-(CH_2)_uCO_2R^{109}$, halogen, cyano, C1-6 alkoxy, $-(CH_2)_x$-[phenyl optionally substituted by from one to five groups R^{113} which may be the same or different], and cycloalkyl containing from thre t six carbon atoms optionally substituted by C1-6 alkyl or $-S(O)_pR^{111}$;

R^{118} is selected from a hydrogen atom, a chlorine, bromine or fluorine atom, methoxy, ethoxy and $-S(O)_pMe$;

R^{119} is selected from a hydrogen atom, a chlorine, bromine or fluorine atom, methoxy and CF_3; and

p and q each independently have the values zero, one or two.

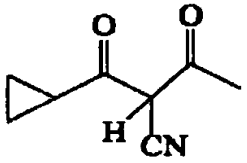
3. A method according to claim 1 or 2 in which the isoxazole or dione herbicide has the general formula (Ib):



(Ib)

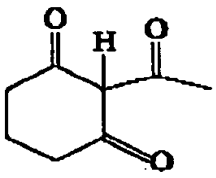
wherein R^{120} is chlorine, bromine or trifluoromethyl; and
R is hydrogen or $-CO_2Et$.

4. A method according to any one of the preceding claims in which a substituted phenyl ring as defined in formulae (I); (Ia); or (Ib) as depicted in claim 1,2 or 3 is attached to a grouping;



5. A method according to claim 4 in which the phenyl ring is substituted by two groups independently selected from halogen, alkyl, $S(O)_p$alkyl (p = 0, 1 or 2) or haloalkyl.

6. A method according to claim 1, 2 or 3 in which a substituted phenyl ring as defined above in formula (I); (Ia); or (Ib) is attached to a grouping;



13. A method according to claim 1 in which the application rate of the benzoylisoxazole and/or dione of formula (I) is from 0.01kg to 2kg per hectare.

14. A method according to any one of the preceding claims in which (a) the herbicidal benzoylisoxazole and/or dione derivative and (b) antidote are applied separately such that the antidote contacts the seed or plant being treated before the herbicidal compound.

15. A herbicidal composition comprising:

(a) a herbicidally effective amount of a benzoylisoxazole and/or dione derivative of formula (I) or an agriculturally acceptable salt or metal complex thereof, optionally in combination with a partner herbicide; and

(b) an antidotally effective amount of an antidote compound;

in association with a herbicidally acceptable diluent or carrier and/or surface active agent.

16. A composition according to claim 15 which comprises the component (a) as a delayed release formulation.

17. A composition according to claim 15 or 16 in which the weight ratio of the compound of formula (I):antidote is from 1:25 to 60:1.

18. A product comprising:

(a) a herbicidally effective amount of a benzoylisoxazole and/or dione derivative of formula (I), or an agriculturally acceptable salt or metal complex thereof; and

(b) an antidotally effective amount of an antidote;

wherein said antidote is antidotally effective to said benzoylisoxazole and/or dione derivative;

as a combined preparation for separate, simultaneous or sequential use in the comtrol of weeds at a locus.

19. A product according to claim 18 as a combined preparation for use in which the antidote contacts the seed or plant being treated before the herbicidal compound.

20. A method according to claim 1 substantially as hereinbefore described.

21. A composition according to claim 15 substantially as hereinbefore described.

22. A product according to claim 18 substantially as hereinbefore described.